INTRODUCTION:

In India, due to its tropical climate, the corrosion problem is more serious than that in cold countries. In fact our economy would be drastically changed if there were no corrosion. Corrosion touches all inside and out side the home, on the road, on the sea, in plant and in aerospace vehicles.

Corrosion is a process that occurs when a material deteriorates due to its interaction with the surrounding environment in which an electrochemical reaction consumes the material through oxidation. As a material corrosively deteriorates, its material properties likewise degrade.[1.] Michael Henthrone[2] said, "The secret of effective engineering lies in controlling rather than preventing corrosion, because it is impossible to eliminate corrosion". Man has continued using metals like iron, aluminum, copper, zinc, brass, lead, nickel etc. to a greater extent.

According to Evans,[3] "corrosion may be defined as destruction of a metal by chemical or electrochemical agencies." H. H. Uhlig[4] has defined corrosion, as "It is the destructive attack of metal by chemical or electrochemical reaction with its environment." Oxidizing tendency of a metal is the driving force for corrosion and it is found in virtually all metals except the very noble metals such as gold and platinum.

Roetheli, cox and littreal[5] pointed out that the high corrosion rate in the strong acid and alkaline solutions can be attributed to the absence of corrosion product films on the metals surface and the easy accessibility of hydrogen ions, hydroxyl ions and oxygen to the metal surface.

Corrosion resistance property of zinc is so important that nearly half the World's annual consumption of the metal about i.e. four million metric tons in all are used to protect steel from rusting. Although, zinc is available in many forms, such as sheet, plate, strip. The uses of zinc are galvanizing, die casting, brass, construction material, zinc chemicals, micronutrient for humans and plants and

pharmaceuticals and cosmetics. The major use of zinc for corrosion control is in the form of coating for steel.

Hydrochloric acid is the solution of hydrogen chloride in water. It is highly corrosive, strong mineral acid and has major industrial uses. With major production starting in the industrial revolution, hydrochloric acid is used in the chemical industries as a chemical reagent in the large-scale production of vinyl chloride for PVC plastic, and MDI/TDI for polyurethane. Hydrochloric acid (HCl) is a monoprotic acid, which means it can dissociate (i.e., ionize) only once to give up one H^+ ion (a single proton). In aqueous hydrochloric acid, the H^+ joins a water molecule to form a hydronium ion, H_3O^+:[6-7]

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

One of the most important applications of hydrochloric acid is in the pickling of steel, to remove rust or iron oxide scale from iron or steel before subsequent processing, such as extrusion, rolling, galvanizing, and other techniques.[8-9]

Use of inhibitors is one of the most important methods widely adopted for corrosion control. Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors.[10-12] According to Hackerman et al.[13-14] the inhibitive properties of a series of secondary aliphatic and cyclic amines in acid media are controlled by the percentage of π - orbital of free electron on the nitrogen atom of these compounds.

R.T.Vashi and H.M.Bhajiwala has studied the corrosion inhibitor of zinc in (HNO_3+HCl) by ethanolamines[15] and by ethylamines[16]. R.T.Vashi and Diksha Naik[17] has studied anisidines as corrosion inhibitors for zinc in phosphoric acid.

Lin Wang et al.[18] has studied the corrosion inhibition of zinc in phosphoric acid solution by 2-mercaptobenzimidazole. However, detailed information about the corrosion behavior of zinc in hydrochloric acid is not much available. Therefore the present study was carried out.

This thesis has been divided into **five** chapters:

Chapter-1 entitled **"Introduction"** describes the importance of corrosion in technology, its definition, corrosion economics, classification of corrosion with suitable examples and their preventive measures, basic principle of electrochemistry, historical review of corrosion, electrochemical and mixed theories of corrosion, factors affecting corrosion, corrosion prevention, physical and mechanical properties of zinc, mechanism of corrosion of zinc, corrosion of zinc in aqueous solution, uses of zinc , reported work , uses of hydrochloric acid and objective of the present study.

Chapter 2 entitled **"Materials and Methods"** includes technique to study the corrosion rate in laboratory condition, the importance of the shape and size of specimen, its surface preparation, cleaning has been described in detail.

Various methods like weight loss, temperature study, open circuit potential and polarization etc. are well explained.

1. ***Weight loss method*** :

Ractangular specimen of the size 4.65 x 2.15 x 0.16 cm having an area of 0.2221 dm^2 of commercial grade zinc (99.96 % Zn, Pb – 0.02% max. Cd – 0.01 % and Fe – 0.01 %) with small hole of 7.9 mm diameter near the upper edge, were used for the determination of corrosion rate. The specimens were degreased with acetone and dried in warm air using air drier and preserve in dessicator till use.

The test specimens were immersed in concentration of 0.01, 0.05, 0.10 and 0.15 M HCl with and without inhibitors. One specimen only suspended by glass hook, in each beaker containing 230 ml of the solution and was open to air at room temperature (301 K) for 24 h. The effect of various inhibitors like ethanolamine, diethanolamine, triethanolamine, ethylamine, diethylamine, triethylamine, o-,m- and p-anisidine and hexamine with 5, 10, 15 and 20 mM concentration were studied to understand the corrosion behavior. After the test, the specimens were

cleaned with 10 % CrO_3 acid solution having 0.2 % $BaCO_3$[19]. Triplicate experiments were performed in each case and mean values of the weight loss was reported as mg / dm^2.

Inhibition Efficiency (I.E.) in percentage has been calculated as follows.

$$I.E.\ \% = \frac{W_u - W_i}{W_u} \times 100 \quad \ldots (1)$$

Where, Wu is the weight loss of metal in uninhibited acid

W_i is the weight loss of metal in inhibited acid.

2. ***Effect of temperature*** :

To study the effect of temperature on corrosion, the specimen were immersed in 230 ml of 0.05 M HCl containg various inhibitors with different inhibitor concentration at 303, 313, 323 and 333 K temperature for a period of 2 h. A thermostate assembly with an accuracy of ± 0.5°C was used. Thermostatic control to within ± 1°C usually be considered satisfactory[20].

Energy of activation (E_a) has been calculated from the slopes of plots of log **ρ** versus 1/T (**ρ** = corrosion rate, T = absolute temperature) and also with the help of the Arrhenius equation.

$$\text{Log } \rho_2 / \rho_1 = E_a/2.303\ R\ [(1/T_1) - (1/T_2)] \quad \text{---------- (2)}$$

Where ρ_1 and ρ_2 are the corrosion rate at temperatures T_1 and T_2 respectively.

The almost similar values of E_a for all inhibitors suggest that the inhibitors are similar in their mechanism of action.

The values of heat of adsorption ($Q_{ads.}$) were calculated by the following equation[21].

$$Q_{ads.} = 2.303\ R[\log (\theta_2/1-\theta_2) - \log (\theta_1/1-\theta_1)] \times [T_1 . T_2 / T_2 - T_1] \quad \text{---------- (3)}$$

Where, θ_1 and θ_2 [$\theta = (Wu - Wi)/Wi$] are the fractions of the metal surface covered by the inhibitors at temperature T_1 and T_2 respectively.

The values of the free energy of adsorption (ΔG°_a), enthalpy of adsorption (ΔH°_a) and entropy of adsorption (ΔS°_a) are calculated.

3. ***Potential measurement*** *:*

For open circuit potential (OCP) measurement, rectangular specimen was used. Potential was measured in 0.01 M and 0.15 M in HCl with an accuracy of ± 0.5 mV with a pH meter against a saturated calomel electrode as a reference electrode. Immediately after the immersion of the specimen, the initial potential value (E_{in}) was recorded. The potential value were continuously recorded after each interval of 2 min. till the constant value (E_{const}) were attained.

4. ***Polarization study*** :

When electrochemical corrosion occures, the current that flows between anode and cathode cause a change in the electrode potential, this change is termed as polarization. For polarization study, metal specimens having an area of 0.0268 dm^2 exposed to 230 ml corrosive solutions. A saturated calomel electrode was used as a reference electrode, platinum as an auxiliary electrode and zinc metal was used as a working electrode. The changes in potential Vs current were measured using potentiostat / galvanostat make Gamry, USA with inbuilt corrosion software. Gelvanostatic polarization has been taken with and without inhibitors in 0.01 M HCl, which indicates both anodic and cathodic polarization.

Chapter 3 entitled **"Results"** starts with the results obtained for the corrosion of zinc in hydrochloric acid. In this chapter, work done on the corrosion of zinc in 0.01, 0.05, 0.10 and 0.15 M HCl in presence and absence of various inhibitors. The results were obtained by the weight loss method, effect of temperature, open circuit potential and polarization method.

It was found that the corroson loss increases with an increase in hydrochloric acid concentration. For example, the corrosion loss was 81.98, 1136.48, 3151.05 and 5221.85 mg/sq.dm in 0.01, 0.05, 0.10 and 0.15 M acid concentration respectively for a period of 24 h at the room temperature. A plot of log p (corrosion loss) vs acid concentration also indicates the same trend.

To determine the effect of temperature on corrosion, weight loss was measured in 0.05 M hydrochloric acid for an immersion period of 24 h at 303, 313, 323 and 333 K. Results indicates that as the temperature increases corrosion loss increases. The results shows that the loss due to corrosion in plain 0.05 M hydrochloric acid was found as 773.98, 949.12, 1594.78 and 2185.05 mg/sq.dm correspond to 303, 313, 323 and 333 K respectively. The result shows that as the temperature increases, the extent of corrosion increases while the I.E. decreases. In 0.05 M HCl p-anisidine at 20 mM concentration shows 98.15, 95.28, 94.06 and 92.82 % I. E. at 303, 313, 323 and 333 K respectively.

A specimen of zinc, when immersed in 0.01 M hydrochloric acid develops a corrosion potential of -944 mV vs calomel as a referance electrode. As the acid concentration was increased, the open circuit potential (OCP) decreases (become more negetive) it is being -965 mV in 0.15 M.

The degree of surface coverage (θ) for different concentration of inhibitors has been evaluated from weight loss. The plots of surface coverage i.e. log (θ/1-θ) vs concentration of the inhibitor (log C) show straight line in all inhibitors tested. A straight line was obtained proving the fact that the adsorption of these compounds on the zinc surface obeys the Langmuir adsorption isotherm. I.E. for all inhibitors studied increases with inhibitor concentration.

The influence of temperature on I.E. for all inhibitors in 0.05 M hydrochloric acid concentration decreases with increase in temperature from 303 to 333 K. It was evident that in all organic substance Q_{ads} values were negative. The value of heat of adsorption varied from -2.23 $kJ.mol^{-1}$ (5 mM Diethylamine) to -100.95 $kJ.mol^{-1}$ (20 mM o-ansidine) in the temperature range of 303 to 313 K.

Study at different temperatures reveals that in almost all the cases mean ΔG_a^o values were negative and ranges from -23.56 to -31.90 $kJ.mol^{-1}$ for organic inhibitors. The value of heat of enthalpy (ΔHa°) and entropy ($\Delta Sa°$) in 0.05 M hydrochloric acid with and without inhibitors are found positive.

Anodic and cathodic galvanostatic polarization curves for zinc in 0.01 M hydrochloric acid alone and containing 20 mM concentration of the various organic substances as inhibitors. The curves show polarization of both the anodes as well as cathodes. In almost all the cases, the I.E. from Tafel plots agree well (within ± 4 %) with the values obtained from weight loss data.

Among inhibitors studied ethanolamine was found to be more effective and exhibited 91.59 % inhibition in 0.15 M acid, while triethylamine was found to be less effective and show 94.28 % inhibition in 0.01 M acid at 20 mM inhibitor concentration.

Chapter 4 entitled **"Discussion"** in this chapter, the action of inhibitors to control corrosion is reported to base either on physical or chemical adsorption on the metal surface has been reported. The structure parameters, inhibitors mechanism.

Mechanism of Corrosion :

Generally, zinc dissolve in hydrochloric acid solution due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,

$$Zn \text{ -------> } Zn^{+2} + 2e^{-} \text{ (anodic reaction)} \quad \text{----------(4)}$$

Reduction reaction is indicated by decrease in valence or the consumption of electrodes, as shown by the following equation.

$$2H^{+} + 2e^{-} \text{ -------> } 2H_{(ads.)} \text{ (cathodic reaction)} \quad \text{----------(5)}$$

Or $$H + H_3O^{+} + e^{-} \text{ -------> } H_2 \uparrow + H_2O \quad \text{----------(6)}$$

At all inhibitor concentration, I.E. of ethanolamines are found in the decreasing order as follows : ethanolamine > diethanolamine > triethanolamine. As the number of lone pairs in the inhibitors increases corrosion also increases. The number of lone pairs increases in the following order 3 (ethanolamine) < 5 (diethanolamine) <7 (triethanolamine). As number of ethanol groups increase on N-atom, it increases crowding around N-atom. This crowding results in strain

which is least in ethanolamine and maximum in triethanolamine. Due to this, the stability of molecule is high in ethanolamine than triethanolamine and so basicity is also reduced. Due to this effect ethanolamine give higher inhibition than diethanolamine and triethanolamine in acid. I.E. in ethylamines are found in the increasing order as follows: ethylamine < diethylamine < triethylamine. In a comparative study of I.E. of isomers of anisidines the I.E was found in the decreasing order is as follows: o-anisidine > p-anisidine > m-anisidine.

The enhanced effectiveness of the inhibitors with concentration is explicable in the light of the extent of adsorption of the inhibitor molecules on the metalic surface. It may be assume that the film formed by the adsorbed molecules of the inhibitors on the metal surface is the sole criteria for lowering the surface area of cathodic and anodic reactions.

At constant acid concentration, the I.E. of all inhibitors increases with increase in inhibitor concentration, e.g. in the case of ethanolamine the I.E. increase from 47.03 to 93.27% as the inibitors concentration increases from 5 mM to 20 mM respectively in 0.1 M acid concentration.

At constant inhibitor concentration, the I.E. decreases with the increase in acid concentration, e.g. at 20 mM inhibitor concentration, the I.E. of m-Anisidine decreases as 96.79, 95.58, 79.86 and 59.69 % with respect to 0.01, 0.05, 0.10 and 0.15 M acid concentration.

Chapter 5 entitled **"Conclusion"** in this chapter, the following facts have been concluded when zinc was immersed in hydrochloric acid in absence and presence of various inhibitors :

- As the acid concentration increases the rate of corrosion increases, while I.E. decreases.
- I.E. increases with the increase in concentration of inhibitors in all acid concentration.

- The degree of surface coverage (θ) was found to increase with inhibitor concentration.
- Plot of log (θ /1-θ) Vs log C shows straight line, which suggest that the inhibitors cover both anodic and cathodic regions through general adsorption following Langmuir isotherm.
- The rate constant k decreases, while half-life ($t_{1/2}$) increases with the concentration of the inhibitor.
- As the temperature increases the extent of corrosion increases, while I.E. was decreases.
- A comparison of 'Ea' values in the presence and absence of inhibitor indicates that 'Ea' values are higher in presence of inhibitor than uninhibited acid, which indicate that the inhibitors are more effective at lower temperatures.
- A study at different temperature shows that values of Q_{ads} are negative for all inhibitor studied. The negative values of Q_{ads} show that the adsorption and hence the I.E. decreases with rise the temperature.
- It is found that the ΔG_a^o values are more positive than –40 $kJmol^{-1}$ indicating that inhibitors are physically adsorbed on the metal surface.
- The values of enthalpy changes ΔH_a^o are positive for all inhibitors studied, which indicate the endothermic nature of the reaction and suggesting that higher temperature favors the corrosion process. The entropy change ΔS_a^o values are positive confirming that the corrosion process is entropically favorable.
- There is a good agreement in the value of I.E. calculated using weight loss data and polarization technique.

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